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Joseph M. Mabry, Ashwani Vij, Brent D. Viers, Wade W. Grabow, Darrell Marchant, & Scott Iacono (AFRL/RZSM); Patrick N Ruth & Isha Vij (ERC)

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9 Antares Road
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Hydrophobic Silsesquioxane Nanoparticles and Nanocomposite Surfaces (Preprint)

An Overview of the Synthesis and Properties of Fluorinated Polyhedral Oligomeric SilSesquioxanes (POSS) and Fluorinated POSS Nanocomposites

Joseph M. Mabry*, Ashwani Vij*, Brent D. Viers, Wade W. Grabow, Darrell Marchant, Scott T. Iacono, Patrick N. Ruth[#], and Isha Vij[#]

Air Force Research Laboratory
[#]ERC Incorporated
Materials Applications Branch
Edwards Air Force Base, CA 93524
e-mail: joseph.mabry@edwards.af.mil, ashwani.vij@edwards.af.mil

Fluorinated Polyhedral Oligomeric Silsesquioxanes are hydrophobic nanoparticles. One compound, **FD_8T_8,** is ultrahydrophobic, possessing a water contact angle of 154°. This is believed to be the most hydrophobic and lowest surface tension crystalline substance known. Analysis of the x-ray crystal structure indicates a large number of Si…F contacts may lead to ultrahydrophobicity.

Introduction

Polyhedral oligomeric silsesquioxanes (POSS) continue to be explored for use in many new applications.[1] Applications include space-survivable coatings,[2-4] and ablative and fire-resistant materials.[5-7] POSS compounds have a rigid, inorganic core and have been produced with a wide range of organic functionality. Due to their physical size, POSS incorporation in polymers generally serves to reduce chain mobility, which often results in the improvement of both thermal and mechanical properties.

The addition of fillers to polymeric matrices is of major technological importance. However, the effects of this process are still not fully understood. Filler addition can impart enhanced scratch resistance, increase thermal or mechanical properties, and improve processing parameters. There has been much effort to optimize the factors in the addition of filler. One factor is filler chemistry. Silicate and carbon black based fillers are quite common. They are often inexpensive and their incorporation into many polymer systems is fairly straightforward. When miscibility is a problem, surface modification of the fillers to further enhance their compatibility is widespread. The silylation of surface silanol groups on silica fillers is a good example. Processing is another factor that has been optimized. The use of high shear to break up large agglomerates or aggregates of nanoscopic particles is common. These approaches yield nanoscopic species with large surface areas, which should favor physisorption and/or chemisorption between the polymer chain and the filler.

A number of reports have detailed that POSS materials can act as reinforcing fillers (or reinforcing comonomers) in a number of nanocomposite systems.[8-10] The results reported herein are somewhat different in that the monodisperse POSS building blocks seem to be rather non-interacting. Specifically, the organic functionality surrounding the silsesquioxane core is composed of fluoroalkyl moieties. Fluoroalkyl compounds are known to be basically inert. This is largely because they are non-polarizable and have low surface free energies. Fluoroalkyl chains are often rigid, due to steric and electronic repulsion. These POSS materials are monodisperse and crystalline. The melting point of the POSS is lower than the processing conditions of the fluoropolymers, so one can safely assume that hard filler effects should not be an issue. In this regard, one may expect that these materials could exhibit small molecule, solvent-like, characteristics. The POSS could be well dispersed and act as molecular ball bearings. This paper will discuss parameters and surface properties of simple blends of FluoroPOSS materials in poly(chlorotrifluoroethylene) matrices.

Experimental

Materials

POSS compounds, (1H,1H,2H,2H-heptadecafluorodecyl)$_8$Si$_8$O$_{12}$ (**FD$_8$T$_8$**) and (1H,1H,2H,2H-tridecafluorooctyl)$_8$Si$_8$O$_{12}$ (**FO$_8$T$_8$**) were prepared using previously reported methods.[11] Poly(chlorotrifluoroethylene) (PCTFE) was obtained from Daikin.

Composite Preparation

Fluoropolymer composites have been prepared by melt blending five, ten, or fifteen weight percent of **FD$_8$T$_8$** or **FO$_8$T$_8$** into PCTFE. All samples were blended in a DACA Micro Compounder for 3 minutes at 100 rotations per minute. The DACA Micro Compounder is a conical co-rotating twin-screw extruder with a bypass allowing the material to circulate for specified times. The capacity of the mixer is 4.5 cm^3. The mean shear rate is approximately 100 s^{-1} and is reported based on a treatment given in literature.[12] The blends were compounded at 280 ºC. Samples for contact angle measurements were prepared into thin films. The films were prepared by compression molding two grams of the polymer-blend extrudate utilizing a Tetrahedron compression molder. The polymer extrudate was placed between two sheets of thick aluminum foil at 10 ºC greater than the compounding temperatures for 10 minutes using one ton of force. All films were less than 0.3 mm thick and about 80 mm in diameter and appeared homogenous and similar to the respective unfilled fluoropolymer.

Contact Angle

Contact Angle analyses were performed on a First Ten Angtroms 110 series system using a syringe metering pump. Deionized water was used as the interrogating liquid. Small drops of water were accurately metered onto a flat surface, and the full screen image of the drop was captured with the frame grabbing software coupled to a CCD camera operating at the optimized zoom and contrast. The contact angle was determined via the software suite or via graphical fitting of the contact tangents in the captured image. Both approaches gave the same nominal value within ± 2 degrees. Only the value of the quasistatic advancing angle is reported.

Results and Discussion

FluoroPOSS Synthesis

FluoroPOSS were produced by the base-catalyzed hydrolysis of trialkoxy silanes. In small-scale syntheses, these compounds tend to condense into T_8 cages (Figure 1), rather than cage mixtures, as has been previously observed in the base-catalyzed synthesis. This is significant because the usual method to produce T_8 cages is the acid-catalyzed hydrolysis of trichlorosilanes, which results in a much longer reaction time and the production of an undesirable acidic byproduct.
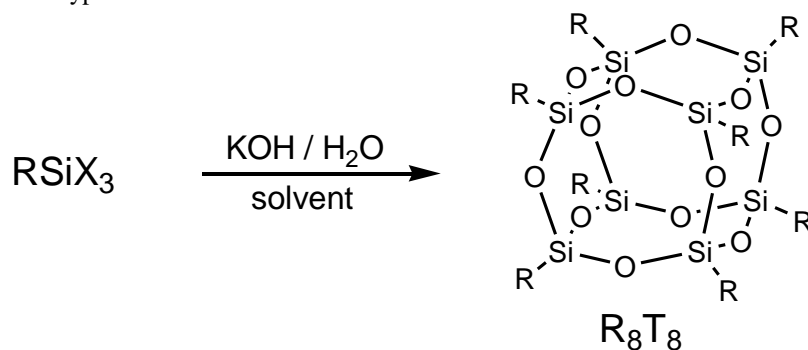

Figure 1. *Synthesis of Fluoroalkyl$_8$T$_8$.*

A variety of FluoroPOSS compounds have been produced, including **FD$_8$T$_8$** and **FO$_8$T$_8$**. Synthesis is currently underway on a number of others. The yields for these reactions are often nearly quantitative. The byproduct is a resinous material that is formed when the condensation is less controlled. The resin is typically removed by extraction.

An interesting occurrence has been observed during the scale-up of the FluoroPOSS synthetic procedure. During large-scale syntheses FluoroPOSS compounds, cage mixtures are often formed. A cage mixture is a combination of cages with eight, ten, and twelve silicon atoms. However, during a purification step involving extraction of the basic catalyst, the cage mixture is converted exclusively to eight-member cages (Figure 2). Because this step involves the dissolving of the compound into a fluorinated solvent, it is believed that the presence of the catalyst allows conversion of the cage mixture to the most thermodynamically stable product. Apparently, in the fluorinated solvent used,

the eight-member cage is the favored product. This conversion can be followed by ^{29}Si NMR spectroscopy. Calculations are underway to confirm this hypothesis.
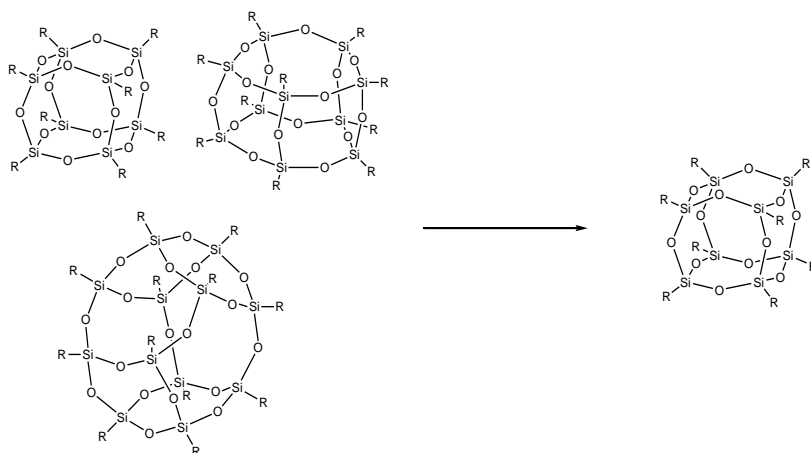

Figure 2. *Redistribution of cage mixture to T_8 cages.*

FluoroPOSS Properties

The properties of the FluoroPOSS compounds are quite interesting. They tend to volatilize at approximately 300 °C, rather than decompose, as is observed with many POSS compounds. The FluoroPOSS are the highest molecular weight POSS yet produced. The **FD$_8$T$_8$** has a molecular weight of 3993.54 g/mol. The density of these materials is also very high, with crystals of the **FD$_8$T$_8$** having a density of 2.067 g/mL.

Various surface properties of the FluoroPOSS compounds have been examined. Water contact angles are a measure of the surface free energy of a surface. As the surface energy decreases, the contact angle increases to a maximum of 180°. The trend observed in the FluoroPOSS compounds is that the surface energy decreases as the length of the fluoroalkyl chain increases. While this may not be surprising, the observed contact angles are unexpectedly high. The **FD$_8$T$_8$** has a water contact angle of 154° (Figure 3), which is approximately 40° higher than the water contact angle of polytetrafluoroethylene (PTFE). The correlation between the chain length and the contact angle is not linear. The contact angle appears to be increasing as the chain length increases.
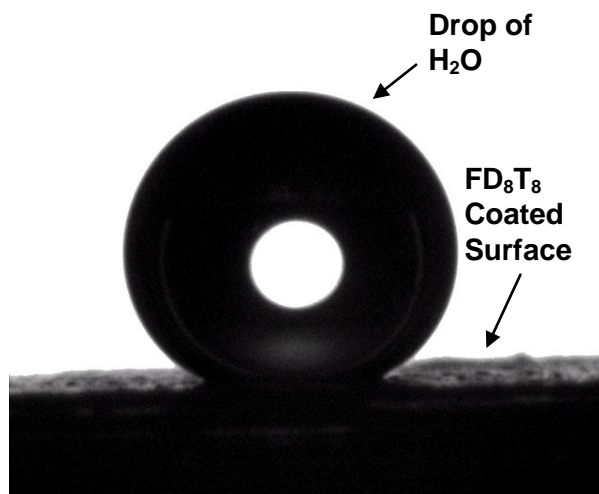
Figure 3. Water drop on surface of FD_8T_8 with a contact angle of 154°.

Solid State Structures of FluoroPOSS

Due to the highly crystalline nature of FluoroPOSS compounds, single crystals were grown from fluorinated solvents. Although these crystals exhibit different morphologies, both materials investigated under this study belong to the triclinic crystal system. Single crystal x-ray diffraction analysis of FD_8T_8 and FO_8T_8 at room temperature did not allow for any reasonable structure solution as there is a large amount of disorder due to the movement of fluoroalkyl chains, which is consistent with observation of large diffused scattering. Our attempts to cool crystals to low temperatures resulted in crystal shattering, probably due to a rapid phase transition. This challenge was overcome by very slow cooling rates. However, at 103 K, the quasi powder-like pattern of diffused scattering disappears, resulting in sharper spots indicating significant ordering due to reduced entropy. The ultrahydrophobic FD_8T_8 exhibits a structure with two molecules within a large asymmetric unit and the fluoroalkyl chains propagating in a zig-zag manner as seen in Figure 4.
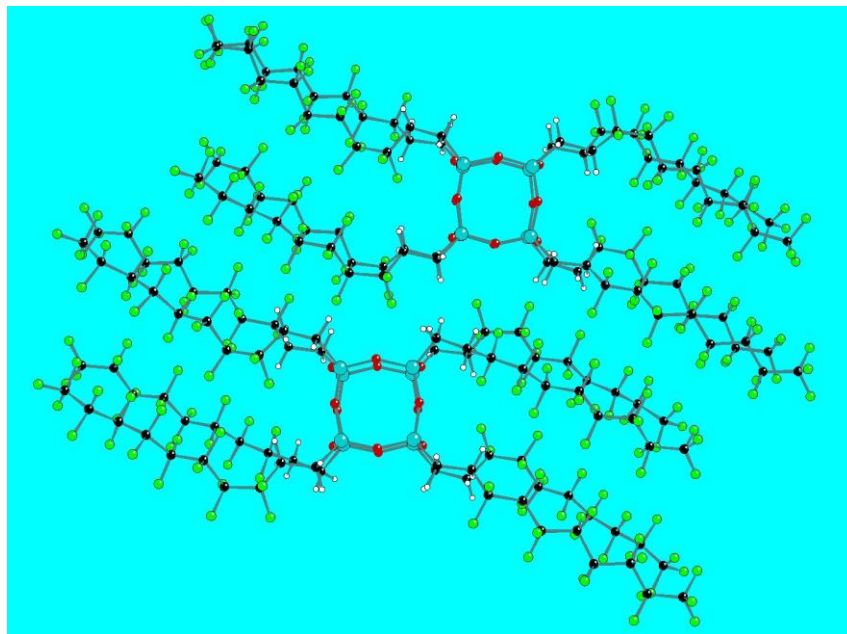
Figure 4. *X-ray crystal structure of FD₈T₈.*

The fluoroalkyl chains adopt both gauche and eclipsed conformations as a result of close intra- and intermolecular Si…F contacts (Figure 5). In addition to these contacts, intermolecular H…F contacts are also observed, which result from lower disorder at 103K. The Si…F contacts are in the range of 3.0-3.5 Å, which is below the sum of van der Waals radii of silicon and fluorine. These contacts cause the non-fluorinated methylene groups to lie flat, along the axis of the rigid fluoroalkyl chains, and increase the packing efficiency of the crystals with an almost parallel arrangement of alkyl chains. This results in the formation of a surprisingly unique structure due to self-assembly.
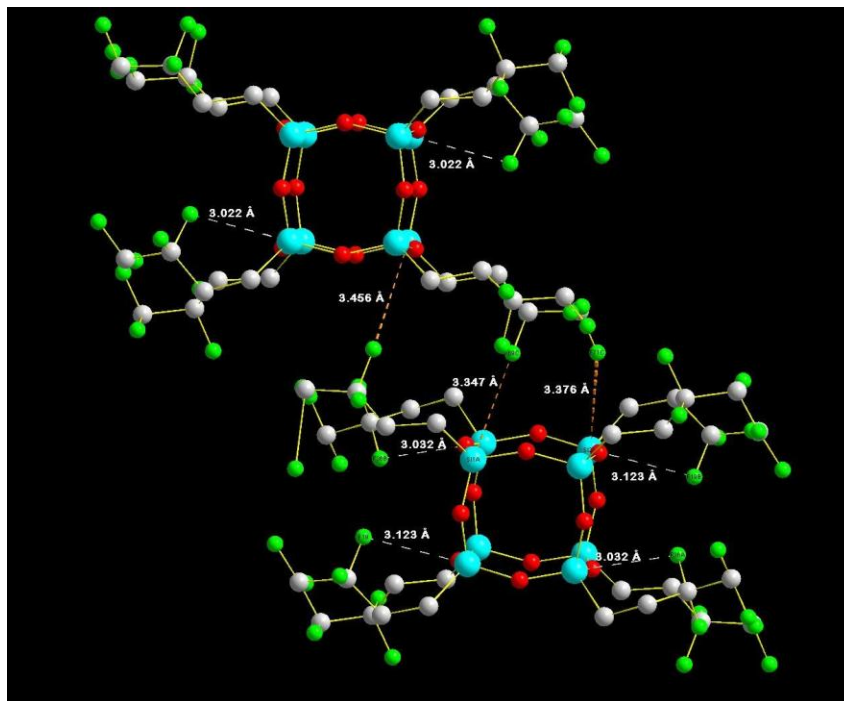
Figure 5. *Cage region of FD₈T₈ structures showing Si-F and H-F contacts.*

POSS Fluoropolymers

The FluoroPOSS compounds mentioned above were blended into poly(chlorotrifluoroethylene). For the purposes of this paper, **FD₈T₈** and **FO₈T₈** blends in PCTFE will be used to describe processing, thermo-mechanical, and surface properties.

Processability

The processability of the samples were compared using torque and load, a measure of the pressure generated in the compounder. The pressure is generated in the mixer due to its conical design. With a constant volume of material compounded and a fixed screw speed, the pressure generated is proportional to the viscosity of the material. The lower the pressure, the lower the viscosity, and the easier the material is to process. The second measure of processability is the

torque output by the motor. This gives an indication of the mechanical energy put into the system and is proportional to the current used by the motor. A similar measure was utilized to characterize the processability of polyethylene and hyperbranched polymer blends.[13] The lower the torque output the more processable the polymer for any given screw speed.

These two measures of the processability of the polymer blends were recorded at 30 second intervals during processing. It was found, within a 95% confidence interval, that the load and torque values were constant for the duration of processing excluding the first 30 sec. Therefore, an average value for both torque and load is assigned to each processing run. In order to investigate the effect of the addition of FluoroPOSS, relative torque and relative load values were computed utilizing the average values in comparison to the average values found for the unfilled resins. Figure 6 shows the relative torque and load values with respect to the weight percentage of POSS added to PCTFE blends. The solid symbols represent the relative torque values whereas the relative load results are illustrated by the open symbols. The square symbols symbolize the results of the **FD$_8$T$_8$** blends and the circular symbols show the **FO$_8$T$_8$** blend results. One will notice that the processability of 10 weight percent of either POSS in PCTFE is improved by greater than 30 percent. In addition, the **FD$_8$T$_8$** exhibits a greater effect on the torque and load for the PCTFE blends.
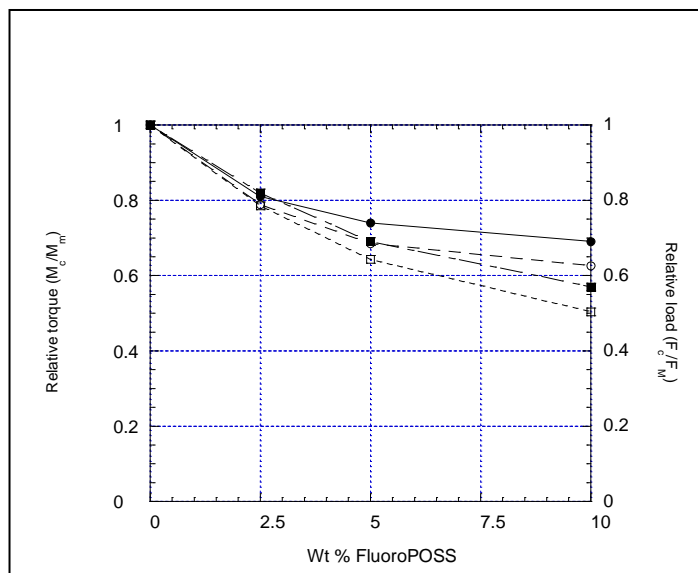

Figure 6. *Effect of FluoroPOSS on torque and load for PCTFE blends.*

Surface Properties

While fluoropolymers are known for their hydrophobicity and low coefficients of friction, incorporation of FluoroPOSS may help to improve these properties even further. Water contact angles are a measure of surface hydrophobicity and provide insight into the free energy of the surface. Contact angles have been obtained on PCTFE nanocomposites containing **FD_8T_8** and **FO_8T_8**. Technologies that may benefit from the blending of FluoroPOSS into fluoropolymers include abrasion resistance, lubricity, anti-icing, and non-wetting applications. Figure 7 shows a drop of water on the surface of a PCTFE film. The contact angle was measured at 88°. Figure 6 also shows a drop of water on the surface of a PCTFE blend containing 10% **FD_8T_8**. The contact angle for this film was measured at 128°. There is a 40° increase in contact angle with just 10% added **FD_8T_8**.
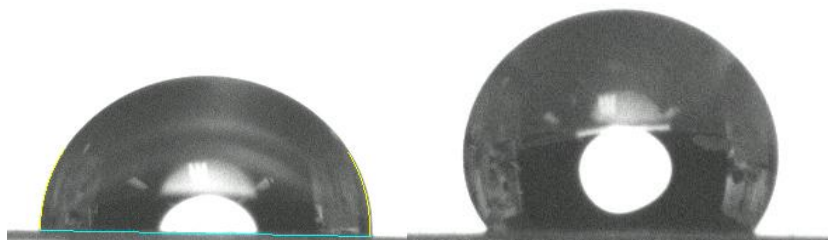

Figure 7. *Water contact angles of 88° and 128° on PCTFE films.*

It has also been observed, as one might expect, that the contact angle increases with increasing weight percent POSS. Contact angles have been obtained on other fluoropolymers as well. All show a similar trend. It should be noted that a surface with a contact angle of 90° or higher is considered a "non-wetting" surface, while a surface with a contact angle below 90° is considered "wetting." Unfilled PCTFE has a contact angle of 88°. Addition of FluoroPOSS produces a "non wetting" surface.

Other Properties

In order to determine the effect of the FluoroPOSS on the mechanical properties on PCTFE, dynamic mechanical analysis (DMTA) was performed. The variation in moduli and glass transition temperatures seen with the addition of FluoroPOSS is small enough to be statistically insignificant.

The level of dispersion of POSS compounds into polymer systems is largely dependent on surface chemistry.   Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM), along with the element mapping capability of SEM, were used to determine nanoparticle dispersion.   These techniques indicate good to excellent particle dispersion in the polymer matrix.

Conclusions

Two fluorinated Polyhedral Oligomeric Silsesquioxanes (FluoroPOSS) have been produced.   The large-scale synthesis results in the production of cage mixtures, which can then be converted to T_8 cages by a redistribution reaction. The FluoroPOSS compounds are hydrophobic, with the **FD_8T_8** possessing a water contact angle of 154°, making it ultrahydrophobic.   Analysis of single crystal x-ray data indicates that molecular scale surface roughness may lead to ultrahydrophobicity.

These compounds have been blended into poly(chlorotrifluoroethylene) (PCTFE). These POSS fluoropolymers may be useful as low friction surfaces or hydrophobic coatings. Contact angle measurements of the POSS fluoropolymers show an improvement of water contact angles over the unfilled materials.   The **FD_8T_8**/PCTFE composite shows a contact angle improvement of 40° over the unfilled material. The low surface energy POSS compounds also appear to act as a processing aid during fluoropolymer processing, significantly reducing both the torque and load measurements in the extruder.   Thermal and mechanical properties of the blended fluoropolymers do not differ significantly from those of the unfilled polymers.

Acknowledgements

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